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THE HYDROLYSIS OF PHOSPHATE ESTERS ON SOLIDS(U) NAVAL
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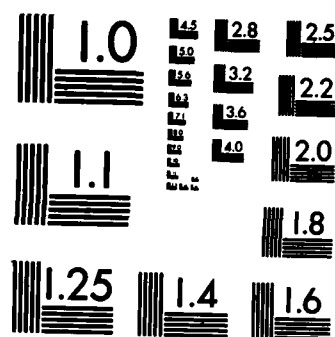


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1. REPORT NUMBER NWC-1	2. GOVT ACCESSION NO. AD-A126119	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) The Hydrolysis of Phosphate Esters on Solids		5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report 10/1/82 - 1/15/83
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Richard A. Hollins		8. CONTRACT OR GRANT NUMBER(s) WR013-01-01 WR014-11-08
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Weapons Center China Lake, California 93555		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 633-846
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research, Code 413 800 North Quincy Street Arlington, Virginia 22217		12. REPORT DATE 2/1/1983
		13. NUMBER OF PAGES 5
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Prepared for publication in JOURNAL OF RESEARCH COMMUNICATIONS (Publication of Chemical Systems Laboratory, Aberdeen Proving Ground, MD)		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Surface Catalysis Hydrolysis Organophosphorus Solid-Supported Reagents		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Several solid materials were examined for hydrolytic activity with organo- phosphorus esters. The solid systems consisted of aliphatic amines surface- immobilized on silica or alumina supports. All materials demonstrated rate enhancements for the hydrolysis of p-nitrophenyldiphenyl phosphate (NPDPF).		

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Task No. NR 633-846

TECHNICAL REPORT NO. 1

The Hydrolysis of Phosphate Esters on Solids

by

Richard A. Hollins

Prepared for Publication

in the

Journal of Research Communications

Naval Weapons Center

China Lake, CA

Februrary 1, 1983

Approved for public release; distribution unlimited.

THE HYDROLYSIS OF PHOSPHATE ESTERS ON SOLIDS

Richard A. Hollins
Naval Weapons Center, China Lake, CA 93555

Several solid materials were examined for hydrolytic activity with organophosphorus esters. The solid systems consisted of aliphatic amines surface-immobilized on silica or alumina supports. All materials demonstrated rate enhancements for the hydrolysis of *p*-nitrophenyldiphenyl phosphate (NPDPP).

Air purification in a toxic environment constitutes an important aspect of personnel protection in relation to industrial chemicals, pesticides and chemical warfare agents. Neat and impregnated activated charcoals have been the most widely studied and used materials in this context¹. In the case of organophosphorus compounds charcoal demonstrates strong but reversible adsorption. Our interest has been to explore alternative solid materials which might show not only adsorption but also concomitant chemical destruction of the toxic substance. We have previously shown that various anion-exchanged forms of Dowex 2-X4 resin enhance the rate of hydrolysis of trimethyl phosphate².

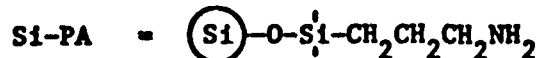
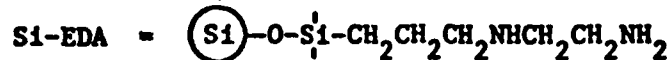
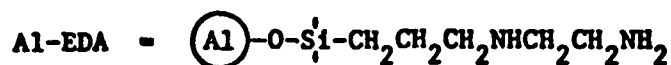
For the investigation of other solid systems we have selected alumina and silica as principal candidate supports for a variety of "reactive" organic moieties as 1) alumina has been shown to react with sarin³ and 2) the chemistry for the surface modification of these materials is extensive⁴.

In our initial studies of these materials we examined three systems:

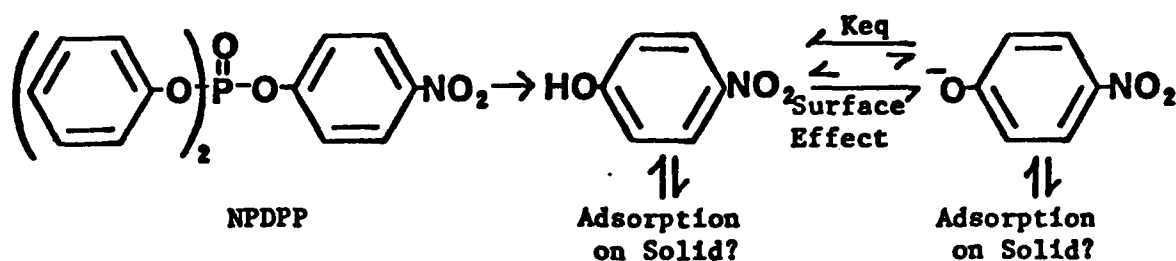
1) An alumina-bound propylethylenediamine (Al-EDA) prepared by treating Woelm I alumina with Dow Corning coupling agent DC 6020. The resulting material contained 0.81 meq/g of amine functionality as determined by titrimetric analysis.

2) A silica-bound propylethylenediamine (Si-EDA) prepared by treating Woelm silica gel with DC 6020. Amine content was found to be 0.96 meq/g.

3) A silica-bound propylamine (Si-PA) prepared by treating Woelm silica gel with Union Carbide A-1100 coupling agent. Amine content was found to be 1.16 meq/g.



Hydrolysis studies were carried out using mixtures of 0.5g of supported reactant and 4mL of a $2.4 \times 10^{-3}\text{M}$ solution of *p*-nitrophenyldiphenyl phosphate (NPDPP) in 30% aqueous ethanol. The extent of reaction was determined by monitoring *p*-nitrophenoxide ion absorbance at 405nm. It was necessary to apply a correction to the observed absorbance vs time plots as the presence of the solid had the effect of augmenting the *p*-nitrophenol dissociation and thus increasing the apparent degree of reaction.



The upper trace in Figure 1 shows the effect of Si-PA on the dissociation of *p*-nitrophenol as compared to its normal equilibrium dissociation indicated by the lower trace. The other solid materials showed similar effects, that of greatly increasing the concentration of *p*-nitrophenoxide over that determined by normal dissociation (at the initial pH of the NPDPP solution).

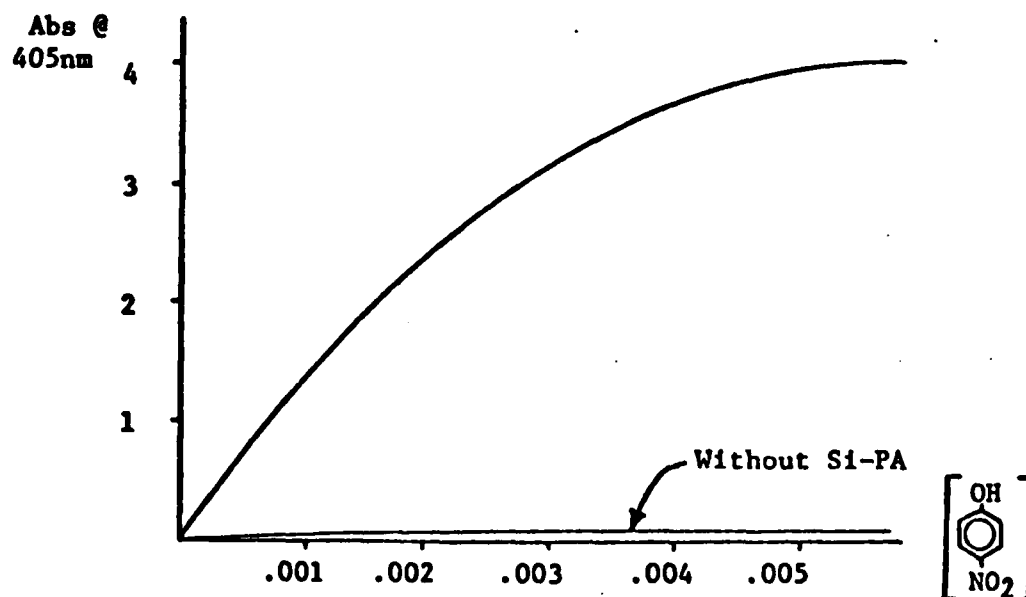


Figure 1. Dissociation of *p*-Nitrophenol by Si-PA

The actual extent of reaction in each hydrolysis study was determined by correlating the observed absorbance (Figure 2) with those values determined for *p*-nitrophenol in the presence of solid (same quantities of solid and solvent as in the reaction).

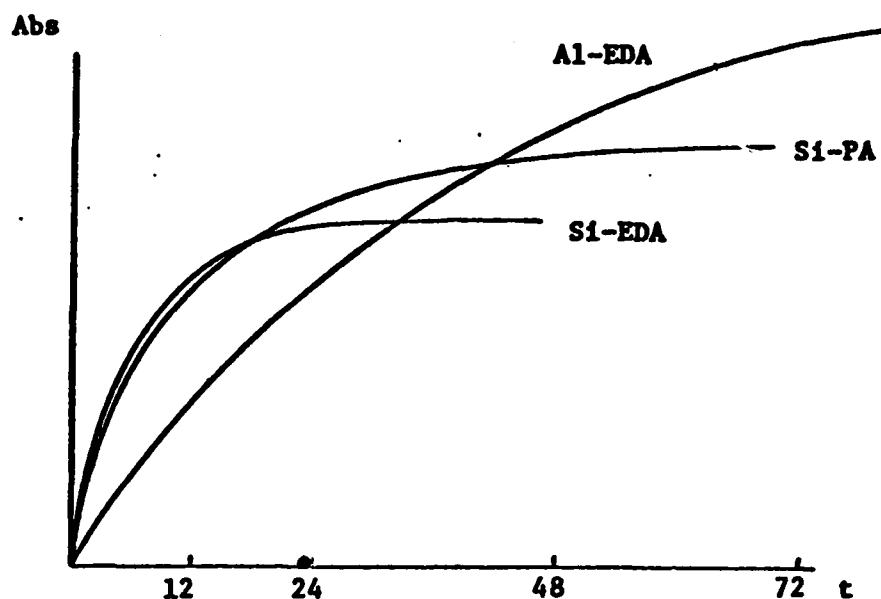


Figure 2. Hydrolysis of NPDPP

The approximate half-lives for these hydrolyses are as follows:

Al-EDA	$T_{1/2} \approx$	24 hrs
Si-PA	$T_{1/2} \approx$	7 hrs
Si-EDA	$T_{1/2} \approx$	4 hrs

CONCLUSIONS

While these rates do not appear to be spectacularly fast, the aqueous NPDPP solutions showed no measurable degree of solvolysis, in the absence of solid reactant, after several weeks of storage, thus enhancement of hydrolysis was very great. Comparison of the Si-EDA material to the others indicates both greater reactivity from the diamine moiety and from the use of silica as a support.

The possibility that a reverse ordering, i.e. alumina better than silica, might occur in the case of fluoro-phosphates was briefly investigated. A crude examination of the relative reactivities of the supported amines with diisopropyl fluorophosphate (DFP) indicated the same qualitative behavior as with NPDPP.

These initial model systems have both demonstrated hydrolysis enhancement for NPDPP and helped to develop the necessary methodology for studying these complex heterogeneous reactions. The supported amines will be further examined as ligands for metal complexes and as functional groups for the attachment of other organic moieties.

ACKNOWLEDGEMENT

This work was supported in part by the Office of Naval Research

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